Long-term stability of cadmium and lead in a soil washing residue amended with MgO-based binders using quantitative accelerated ageing

Zhengtao Shen[1,2], Deyi Hou[1,*], Wendi Xu[1], Jingzhuo Zhang[1], Fei Jin[3], Bin Zhao[1], Shizhen Pan[1,4], Tianyue Peng[1], Daniel S. Alessi[2]

1 School of Environment, Tsinghua University, Beijing 100084, China

2 Department of Earth and Atmospheric Sciences, University of Alberta, Edmonton T6G 2E3, Canada

3 School of Engineering, University of Glasgow, Glasgow G12 8QQ, UK

4 School of Chemical and Environmental Engineering, China University of Mining and Technology, Beijing 100083, China

*Corresponding author: Deyi Hou, E-mail: houdeyi@tsinghua.edu.cn

Abstracts: A soil washing residue (SWR) (containing 90% clay, cadmium (Cd^{2+}) of 132 mg/kg, lead (Pb^{2+}) of 3410 mg/kg) was stabilized with MgO (M) and MgO + bioapatite (MB) respectively at a dosage of 5% in w/w. The stability of the metals in original and amended SWRs was assessed after immediate treatment and using a laboratory accelerated ageing method simulating 26, 52, 78 and 104 years in field conditions. The dissolved Cd^{2+} and Pb^{2+} from the SWR in Toxicity Characteristic Leaching Procedure (TCLP) leachates significantly reduced (by 96.84-99.06%) by both amendments after immediate treatment. The stabilization remained effective within simulated 26 years as the TCLP leached Cd^{2+} and Pb^{2+} kept below regulatory levels. This immobilization was mainly due to the increased non-bioavailable Cd^{2+} and Pb^{2+} from sequential extraction tests in SWR by the amendments. At simulated 52 years, the TCLP leached Cd^{2+} from M and MB exceeded regulatory level by 106% and 1% respectively. Large amounts of Cd^{2+} and Pb^{2+} were leached out by 36.74-48.18% regardless of the treatments at simulated 104 years. Although bioapatite can significantly aid the stabilization of metals by MgO, the stabilization effectiveness for both treatments diminished at simulated 52 years and from 52 to 104 years.

Keywords: soil washing residue, accelerated ageing, heavy metal, Cd and Pb stabilization, MgO

1 Introduction

Soil washing is one of the few remediation technologies that result in permanent removal of contaminants from soil. It has been widely used in practices globally such as in the United States (Griffiths, 1995), the United Kingdom (e.g., the 2012 London Olympic Park) (Hou et al., 2015) and China (Song et al., 2018). It has been considered as a relatively sustainable remediation technique because it facilitates the reuse of contaminated soil and avoids the import of fill materials. Although soil washing possesses great advantages in the thorough clean-up of the contaminated sites and the reuse of the clean soil over stabilization-based remediation technologies, chemical extraction (one form of soil washing) could be very expensive: e.g., $ 358-1717 m^{-3} (Dermont et al., 2008) compared with $ 50-330 m^{-3} for stabilization/solidification (USEPA, 2010).

The main costs in chemical extraction are from the large amounts of solvents used to thoroughly extract contaminants (typically for heavy metals) from the soil (regardless of soil constitutes). Alternatively, physical separation (another form of soil washing) is far more cost-effective (($ 70-187 m^{-3}) compared with chemical extraction (Dermont et al., 2008). Physical separation uses a range of technologies (e.g., mechanical screening, hydrodynamic classification and gravity concentration) to remove weakly bonded heavy metals and separate the cleaned coarse particles from the soil (Dermont et al., 2008). The cleaned

coarse particles (typically > 50-70% in w/w) can be reused; however, this process also enriches heavy metals in the remaining fine soil particles. The soil washing residue (SWR) (the clay particles concentrated with heavy metals) is of great risk to the environment (Shen et al., 2018a). A recent study observed that Cd^{2+} and Pb^{2+} in a soil washing residue (containing 90% clay) exceeds Toxicity Characteristic Leaching Procedure (TCLP) (based on USEPA 1311) regulatory level regardless of biochar stabilization (Shen et al., 2018a). Stabilizing metals in clay-rich soil is always challenging due to the competitive adsorption between clay and binders/sorbents – the clay of the soil will competitively adsorb the metals against the amendments; however the adsorbed metals on clay particles are exchangeable and mobile in the long term (Shen et al., 2016a). Therefore, it is important to devise effective ways to stabilize heavy metals in SWR; however, such efforts are very limited (except (Shen et al., 2018a)).

When stabilization is implemented, another crucial issue is to ensure its long-term effectiveness. Short-term stabilization of heavy metals is usually achievable. However, environmental factors such as rainfall wash, groundwater flow, wet-dry cycles, freezing-thawing cycles, plant growth and soil microbes may affect stabilization in the long term. The long-term effectiveness of stabilization is critical for the sustainability of remedial alternatives; because the lack of long-term effectiveness implies the necessity

of repeated treatment, which would render significant higher life cycle secondary impact. Such shortcoming is a major obstacle in achieving green and sustainable remediation of contaminated land (Hou and Al-Tabbaa, 2014).

Despite a few long-term monitoring on field stabilized sites (Oustriere et al., 2016; Shen et al., 2016b), a more realistic way to assess the long-term effectiveness of stabilization is to simulate the long-term field conditions by short-term accelerated ageing experiments in laboratory. Although numerous physical, chemical and biological ageing methods have been used in extant research (Hale et al., 2011; Rechberger et al., 2017; Suzuki et al., 2013), there is a research gap regarding the correlation between artificial short-term ageing and actual aging in the field. Although an acidic solution was prepared and used for Pb^{2+} leaching tests of a MgO-based-material amended contaminated soil to represent the influence of 100-year field ageing (Suzuki et al., 2013), the time-dependent effectiveness of the stabilization across the simulated 100 years was unclear. For instance, even if the simulated 100-year ageing revealed that the soil exceeded the regulatory limit after simulated 100 years, it was still unclear which year was the critical point where the soil started to exceed the limit and pose risks.

In this context, a SWR was stabilized with MgO-based binders (the selection of the binders is detailed in section 2.2). An accelerated ageing method was modified and developed from (Suzuki et al., 2013) to simulate natural rain in

102 field conditions across 104 years with an interval of 26 years. This research
103 aims to shed lights on two important issues: 1) the stabilization of SWR which
104 is a problematic contaminated soil; and 2) the assessment of the stability of
105 heavy metals in amended SWR in the long term.

106 ## 2 Materials and methods

107 ### 2.1 Soil and amendments

108 The SWR is from a contaminated site in Guangzhou, China that belongs to
109 one of the biggest steelmaking companies in China. The original site soil
110 contains heavy metals: Cd, Hg, As, Pb, Cr, Cu, Zn, Ni, Se, Co, V, Sb (at
111 varying concentrations up to 54100 mg/kg), polycyclic aromatic hydrocarbons
112 (≤ 4190 mg/kg) and petroleum hydrocarbons (≤ 44000 mg/kg). During
113 2015-2016, a thorough clean-up was implemented on site using soil washing
114 (physical separation) and thermal desorption. Detailed site remediation
115 process can be found in (Shen et al., 2018a). The SWR that concentrates
116 heavy metals was collected for the present study. The properties of SWR can
117 be found in (Shen et al., 2018a) and are shown in Table 1.

118 Table 1 Properties of the soil washing residue (SWR) (Shen et al., 2018a).

Properties	value
pH	9.14 ± 0.02[a]

Total organic matter content (%)	3.46
Clay (0-002 mm) (%)[b]	89.68 ± 0.23
Silt (0.002-0.05 mm) (%)[b]	10.21 ± 0.11
Sand (0.05-2 mm) (%)[b]	0
Cd^{2+} (mg/kg)	132 ± 6
Pb^{2+} (mg/kg)	3410 ± 210

(a-mean ± standard deviation, n=3, b-based on United States Department of Agriculture System)

A previous study shows that leached Cd^{2+} (3.83 mg/L) and Pb^{2+} (10.49 mg/L) from the SWR exceeds TCLP regulatory levels (1 mg/L for Cd^{2+} and 5 mg/L for Pb^{2+}, respectively) (Shen et al., 2018a). This suggests the SWR is of great risk to the environment and stabilization is needed. Therefore, a pre-trial was conducted in this study to investigate the effects of different amendments in reducing the leachability of Cd^{2+} and Pb^{2+} in TCLP. It was observed from the pretrial that MgO was the only amendment that can reduce both Cd^{2+} and Pb^{2+} in SWR to below TCLP regulatory levels. Bioapatite (BAp) ranked second best in reducing Cd^{2+} and Pb^{2+} concentrations in TCLP leachates.

The mechanisms of MgO in stabilizing heavy metals in soils have been investigated in relatively short terms previously (Chimenos and Fern, 2004;

Wang et al., 2016). Elevated pH (liming effect) and its hydration products (brucite ($Mg(OH)_2$)) were proposed to contribute to heavy metal immobilization by precipitation and adsorption (Chimenos and Fern, 2004; Wang et al., 2016). However, in the long term, especially considering the effect of acidic rain water in field conditions, the liming effect has the risk to be diminished and the precipitated metals may be dissolved gradually. Therefore, bioapatite was proposed to aid MgO for metal stabilization. The hypotheses are: bioapatite may form metal-phosphate which is of extremely low solubility and high pH-resistance (Q. Li et al., 2017; Z. Li et al., 2017; Shen et al., 2018a) to aid the long-term stability of heavy metals in SWR. The MgO and bioapatite were sieved through #200 mesh (< 0.075 mm) and stored in sealed sample bags. The properties of MgO and bioapatite are shown in Table 2. The producers of these amendments and the testing procedures of their properties are shown in supporting information.

Table 2 Properties of MgO and bioapatite.

	MgO	Bioapatite
pH	10.79 ± 0.01[a]	8.53 ± 0.05
BET surface area (m^2/g)	6.45	1.24
MgO (%)	98.84	1.40

Na_2O (%)	N.D.[b]	0.56
Al_2O_3 (%)	0.27	N.D.
CaO (%)	0.27	50.90
SiO_2 (%)	0.11	N.D.
P_2O_5 (%)	0.01	45.35
F (%)	N.D.	3.00

147 (a - mean ± standard deviation, b - not detected)

148 2.2 Amendment and accelerated ageing

149 Two types of amendments were applied to the SWR which results in three soil
150 samples, i.e., the original SWR without any amendments (C); SWR + 5% (in
151 dry w/w, hereafter) MgO (M); and SWR + 5% MgO + 5% BAp (MB). The
152 selection of the dosage (5%) was based on a previous study (Shen et al.,
153 2018a). The moisture content of all samples were 40% w/w based on a
154 previous study (Shen et al., 2018a). After preparation, the samples were
155 incubated in a moisture chamber with ~100% humidity for 24 h at room
156 temperature and then a certain amount of the samples was collected as the
157 representative samples after immediate treatment at 0 year.

158 A quantitative accelerated ageing was applied to all the rest samples. The
159 ageing method was developed from (Suzuki et al., 2013). Rain water is always

160 acidic and the mobilization of the metals in soil by the H^+ in rain water is one of
161 the major factors affecting their stability in the long term. If assuming 1 m^3 of
162 soil (assuming a dry density of 1.3 g/cm^3) receives 2000 mm annual rainfall
163 over an area of 1 m^2 (assuming a pH of 5.6 which represents the pH of natural
164 rain water (Du et al., 2017)), then it can be calculated that 1 g of dry soil
165 receives 1.538 mL of rain water annually.

166 CO_2 saturated water (pH 5.6) was prepared by adding CO_2 to deionized water
167 for 15 min at 0.3 MPa of input pressure to simulate natural rain water (Du et al.,
168 2017). Then the dry sample was mixed with the CO_2 saturated water at a
169 solid/liquid ratio of 1:10 (g/mL) and stirred at 75 rpm for 8 h. Based on the
170 calculation, this process simulates 6.5 years of accumulated H^+ from natural
171 rain water that the soil receives in field conditions. After each wetting process,
172 the mixture stood for 1 h and the supernatant was discarded. The sediments
173 were oven dried at 40 °C to reach a constant weight. Then the same wet and
174 dry cycle was repeated. Therefore, every four wet-dry cycles simulate 26 years
175 of accumulated H^+ from natural rain water the soil receives in field conditions.
176 A total of 16 wet-dry cycles was conducted in this study. The term “simulated
177 26 (or 52, 78 and 104) years” will be used throughout the paper to represent
178 the simulated years of the accelerated aging in terms of H^+ reception from
179 natural rain water. The limitation of this ageing method is discussed in section
180 3.5.

2.3 Chemical analysis

After each four wet-dry cycles, a certain amount of soils from each sample was collected and oven dried at 40 °C to reach a constant weight, to represent control (C), MgO amended (M) and MgO + BAp amended (MB) SWRs at simulated 26, 52, 78 and 104 years. Together with the soils after immediate treatment, the soil pH, TCLP characteristics, soil total metal concentrations, metal fractions of the samples, scanning electron microscopy (SEM) with energy dispersive X-ray (EDX) spectroscopy tests, X-ray diffraction (XRD) and X-ray fluorescence (XRF) tests were determined. The soil pH was recorded with a solid/liquid ratio of 1:5 based on ISO 10390:2005. TCLP was performed to assess the mobility and environmental risks of Cd^{2+} and Pb^{2+} in the samples based on USEPA 1311. Briefly, the soil and buffer solution (HOAc/NaOAc, pH 2.88) were mixed at a solid/liquid ratio of 1:20 in a polyethylene tube. The mixture was shaken at 250 rpm for 18 h before filtration. Concentrations of Cd^{2+} and Pb^{2+} in the filtrate were measured by inductively coupled plasma mass spectrometry (ICP-MS) (Thermo Fisher XSERIES 2) after dilution and acidification. Soil total metal concentration was determined by microwave digestion followed by ICP-MS measurement based on USEPA method 3051. Briefly, 0.25 g of soil was mixed with 9 mL concentrated nitric acid (68% w/w) and 3 mL concentrated hydrochloric acid (36% w/w). The mixture was digested for 25 min (5 min (120°C) + 10 min (150 °C) + 10 min (180 °C)) in a MARS6

202 Microwave digestion system (CEM, United States) before dilution and
203 acidification for ICP-MS measurement. A simplified three-step sequential
204 extraction (adapted from (Shen et al., 2018b)) was applied to assess the
205 fractions of Cd^{2+} and Pb^{2+} in the samples. Briefly, the metals were partitioned
206 into three fractions through the following steps:

207 Step 1 – exchangeable fraction: The soils (1 g) was extracted with 8 mL of 0.5
208 M $MgCl_2$ (adjusted to pH 7.0 using NaOH or HCl) and shaken for 20 min at
209 room temperature;

210 Step 2 – acidic soluble fraction: The solid residue from Step 2 was extracted
211 with 8 mL of 1 M NaOAc (adjusted to pH 5.0 with HOAc) and shaken for 5 h at
212 room temperature;

213 Step 3 – non-bioavailable fraction: soil total metal concentration deducted by
214 fraction 1 and 2.

215 In sequential extraction, shaking in step 1 and 2 was performed at 250 rpm.
216 Following each step, the samples were centrifuged at room temperature. The
217 supernatant was then collected and filtered through a 0.45 μm filter and
218 acidified and diluted when necessary before analysis with ICP-MS to
219 determine the metal concentration. The remaining solid sample was washed
220 with 20 mL deionized water prior to the next extraction step, and the washing
221 solution was discarded after centrifugation.

The SEM/EDX analyses of the samples (coated with platinum) were performed to investigate the morphology of the samples and to aid the mechanistic interpretation. SU8010 Ultra-High Resolution (1.0 nm) Scanning Electron Microscope (Hitachi, Japan) was used for SEM/EDX tests. XRD tests were performed to examine the mineralogical characteristics of the samples using a Bruker D8 Advance diffractometer (Cu-Ka; λ = 1.54060 Å; 40 kV; 40 mA; scanned from 10-80 º at a speed of 0.02 º/s). Mg concentrations in soils were tested by an X-ray fluorescence spectrometer (XRF-1800, Shimadzu, Japan).

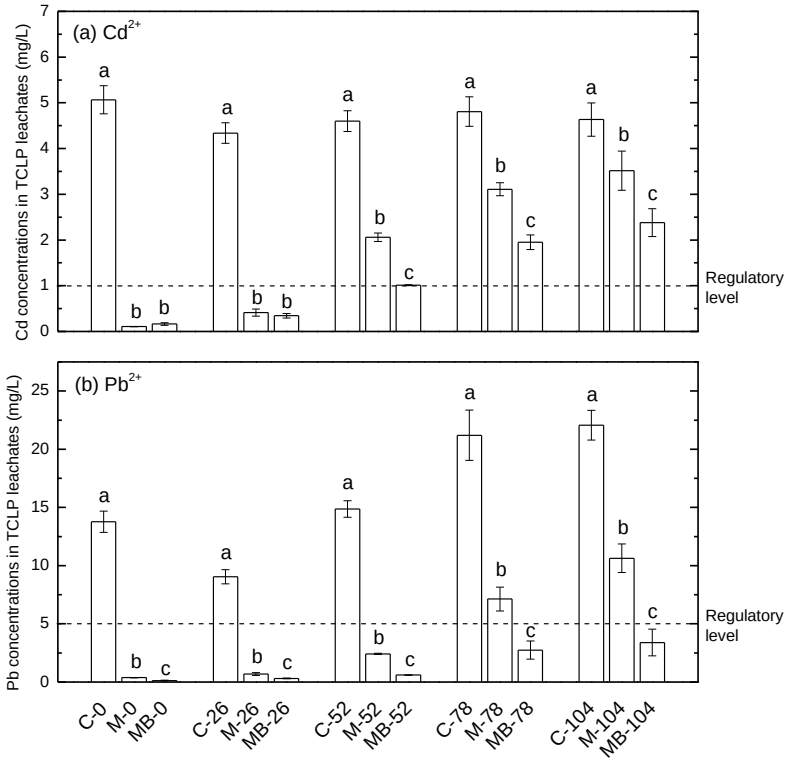
2.4 Statistical analysis

TCLP tests were conducted in triplicates. Tests determining soil pH, total metal concentrations and fractions were conducted in duplicates. Means and standard deviations were presented for each experiment. The difference between two groups was evaluated by two-tailed T test at the significance level of 0.05. Different lower-case letters were used to indicate significant differences between two data groups. If the lower-case letters of two groups contain no same letter, it means the two groups are significantly different ($P < 0.05$). If they contain any same letter, it means they are not significantly different ($P \geq 0.05$). The statistical analysis was conducted using Microsoft Excel 2016.

3 Results and discussion

3.1 TCLP results

The dissolved Cd^{2+} and Pb^{2+} from original and amended SWRs in TCLP leachates are shown in Figure 1. The amendment effectively reduced the leached Cd^{2+} and Pb^{2+} in the SWR to below TCLP regulatory levels after immediate treatment at 0 year. Cd^{2+} in TCLP leachates reduced by 97.83% and 96.84% respectively; similarly, Pb^{2+} in TCLP leachates reduced by 97.24% and 99.06% respectively by MgO and MgO + BAp amendments. At simulated 26 years, the amendments remained effective as the dissolved Cd^{2+} and Pb^{2+} from the amended SWRs in TCLP leachates were still below the TCLP regulatory levels.



253 Figure 1. Cd^{2+} and Pb^{2+} concentrations (mg/L) in TCLP leachates of original
254 and amended soil washing residues (C – control, M – 5% MgO, MB – 5% MgO
255 + 5% Bioapatite; 26, 52, 78 and 104 indicate the simulated years in field
256 conditions; 0 means after immediate treatment; different lower-case letters
257 indicate significant differences between two data groups)

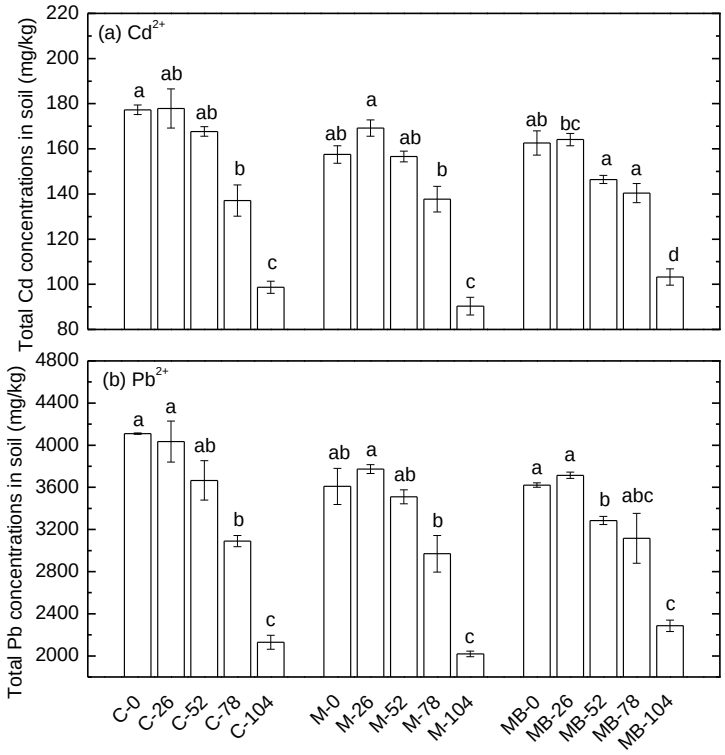
258 Accelerated aging increased the TCLP leached Cd^{2+} and Pb^{2+} from the
259 amended SWRs from simulated 26 to 52 years. At simulated 52 years, Cd^{2+} in
260 M significantly exceeded regulatory level (by 106%), whereas Cd^{2+} in MB just
261 slightly exceeded TCLP regulatory level (by 1%), suggesting that the addition
262 of BAp significantly enhanced the immobilization of Cd^{2+} by MgO. In contrast,
263 TCLP leached Pb^{2+} from both M and MB was still below regulatory level,
264 although increased compared with simulated 26 years. TCLP leached Cd^{2+}
265 and Pb^{2+} from both M and MB continued to increase from simulated 52 to 104
266 years. At simulated 104 years, TCLP leached Cd^{2+} from M and MB exceeded
267 regulatory level by 252% and 138% respectively; TCLP leached Pb^{2+} from M
268 exceeded regulatory level by 113%, whereas that from MB remained below
269 regulatory level, which again suggests the enhancement of metal
270 immobilization by the addition of BAp.

271 In general, for the original SWR, accelerated ageing simulating 104 years did
272 not significantly change the TCLP leached Cd^{2+}, but increased Pb^{2+} by 60.28%.
273 In contrast, it significantly increased TCLP leached Cd^{2+} (by 3100% and

1388%) and Pb^{2+} (by 2697% 2515%) in M and MB. The presence of BAp significantly reduced the Cd^{2+} and Pb^{2+} in TCLP leachates compared with MgO-alone amendment. The TCLP leached Cd^{2+} in the control samples was not significantly different during the simulated 104 years; in comparison, the TCLP leached Pb^{2+} generally increased. The decrease of TCLP leached Pb^{2+} from 0 to simulated 26 years in the control samples was likely due to the heterogeneity of the soil.

3.2 Total metal concentrations

Figure 2 shows the variation of total metal concentrations in original and amended SWRs during the simulated 104 years. Accelerated ageing significantly deceased the total Cd^{2+} and Pb^{2+} concentrations in SWR regardless of the stabilization amendments at simulated 104 years. Specifically, total Cd^{2+} in C, M and MB decreased by 44.07%, 43.04% and 36.81% respectively; similarly, total Pb^{2+} decreased by 48.18%, 44.04% and 36.74% respectively.



289

290 Figure 2. Total Cd^{2+} and Pb^{2+} concentrations (mg/kg) in original and amended
291 soil washing residues (C – control, M – 5% MgO, MB – 5% MgO + 5%
292 Bioapatite; 26, 52, 78 and 104 indicate the simulated years in field conditions;
293 0 means after immediate treatment; different lower-case letters indicate
294 significant differences between two data groups)

295 At simulated 26 years, the total Cd^{2+} and Pb^{2+} concentrations in the original
296 and amended SWRs were not significantly changed. Slight decrease of total
297 Cd^{2+} and Pb^{2+} concentrations in the original and amended SWRs occurred at
298 simulated 52 years although not statistically significant, which became more
299 and more significant from simulated 52 to 104 years. At simulated 104 years,
300 the total Cd^{2+} and Pb^{2+} concentrations in the original and amended SWRs

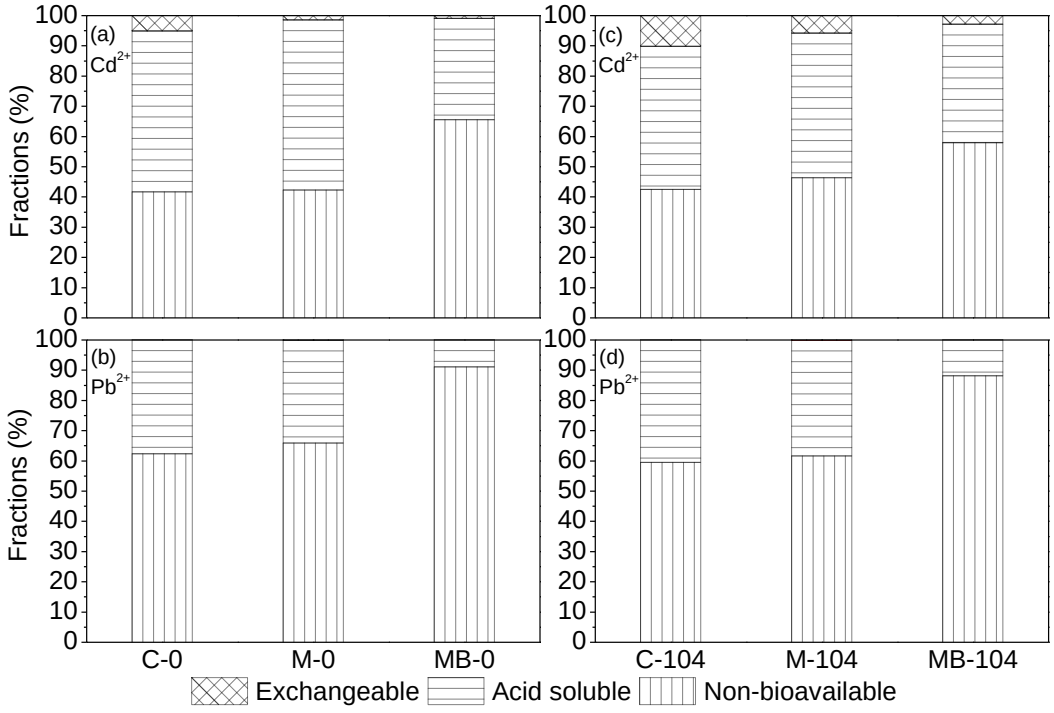
301 reduced by 36.74-48.18%. This suggests a significant mobilization of Cd^{2+} and
302 Pb^{2+} by accelerated ageing from 52 to 104 years, which coincides with the
303 finding that TCLP leached Cd^{2+} and Pb^{2+} from amended SWRs started to
304 significantly increase (Figure 1) at simulated 52 years and later. Cd^{2+} and Pb^{2+}
305 concentrations in TCLP leachates were not significantly changed, compared to
306 the significant reduction of their total concentrations in the original SWR. This
307 was due to that Cd^{2+} and Pb^{2+} in the SWR were originally very mobile, as can
308 be seen from Figure 1.

309 3.3 Stabilization mechanisms

310 Two questions can be raised based on the TCLP and total metal
311 concentrations results: 1) How can the amendments decrease the mobility of
312 Cd^{2+} and Pb^{2+} in the SWR to stay below TCLP regulatory levels after
313 immediate treatment? What are the immobilization mechanisms? 2) How does
314 the accelerated ageing mobilize Cd^{2+} and Pb^{2+} in the amended SWRs and
315 lead to the failure of stabilization in the simulated long term? Based on these
316 two questions, sequential extraction tests were carried out to investigate the
317 mechanisms.

318 Figure 3 shows the fractions of Cd^{2+} and Pb^{2+} in the original and amended
319 SWRs. Exchangeable Pb^{2+} in all samples was negligible. After immediate
320 treatment, MgO amendment significantly decreased exchangeable Cd^{2+} (from
321 5.13% to 1.41%) and slightly increased non-bioavailable Cd^{2+} (41.67% to

322 42.24%) and Pb^{2+} (42.52% to 46.39%). MgO + BAp amendment further
323 decreased exchangeable Cd^{2+} to 0.91% and significantly increased
324 non-bioavailable Cd^{2+} to 65.50% and Pb^{2+} to 57.91%. Exchangeable fraction
325 represents the most mobile metals in soil which is of greatest environmental
326 risk, whereas non-bioavailable fraction is generally stable (Shen et al., 2017b).
327 The decrease in exchangeable Cd^{2+} and increase in non-bioavailable Cd^{2+} and
328 Pb^{2+} indicate a strong immobilization of the metals by the amendments after
329 immediate treatment. This also explains the sharp decrease of TCLP leached
330 Cd^{2+} and Pb^{2+} after both amendments compared with original SWR after
331 immediate treatment.



332

333 Figure 3. Cd^{2+} and Pb^{2+} fractions (%) in original and amended soil washing
334 residues at simulated 0-year (a and b) and 104-year (c and d) (C – control, M –

335 5% MgO, MB – 5% MgO + 5% Bioapatite; 0 and 104 indicate after immediate
336 treatment and at 104 simulated years in field conditions, respectively).

337 At simulated 104 years, the amended SWRs still revealed lower fractions of
338 exchangeable Cd^{2+} and higher fractions of non-bioavailable Cd^{2+} and Pb^{2+},
339 although a large portion of Cd^{2+} and Pb^{2+} in all samples have been leached out
340 by accelerated ageing. Therefore, the TCLP leached Cd^{2+} and Pb^{2+} were lower
341 in the amended SWRs compared with the original SWR at 104 years. MgO +
342 BAp generally show better immobilization than MgO alone due to less
343 exchangeable Cd^{2+} and more non-bioavailable Cd^{2+} and Pb^{2+} (Figure 3c&d).
344 Therefore, the TCLP leached metals were lower in MB than in M generally
345 (Figure 1), and MB retained more Cd^{2+} and Pb^{2+} than M (103 vs 90 mg/kg for
346 Cd^{2+}, 2290 vs 2020 mg/kg for Pb^{2+}) (Figure 2) at simulated 104 years.

347 Similar findings were observed in a previous study (Suzuki et al., 2013), where
348 the addition of MgO to soil significantly decreased exchangeable Pb^{2+} (from
349 ~12% to ~0%) and increased residual Pb^{2+}, which is non-bioavailable. This
350 immobilization was attributed to the increased alkalinity by the hydration of
351 MgO to $Mg(OH)_2$ and consequently the precipitation of Pb^{2+} to hydrocerussite
352 (Suzuki et al., 2013). Therefore, the increased pH by MgO addition and its
353 strong buffering capacity are considered a major mechanism for MgO to
354 stabilize metals in soils (Chimenos and Fern, 2004; Sanderson et al., 2015;
355 Suzuki et al., 2013). In addition, due to the strong buffering effect of MgO, the

356 extraction solvent in step 2 of sequential extraction may not be able to dissolve
357 the $Mg(OH)_2$ and mobilize the metals. This explains why large amounts of Cd^{2+}
358 and Pb^{2+} remained in the amended SWRs after step 2 of sequential extraction.

359 BAp can form pyromorphites with Pb^{2+}, which is very stable in soils (Shen et al.,
360 2017a). It can also form metal phosphate with Cd^{2+}, which is of low
361 bioavailability (Sneddon et al., 2006). Therefore, the presence of BAp can
362 immobilize Cd^{2+} and Pb^{2+} and further increase non-bioavailable Cd^{2+} and Pb^{2+}
363 fractions compared to MgO-alone amendment. In addition, the presence of
364 MgO may aid the formation of pyromorphite (Sanderson et al., 2015) and
365 thereby further enhance the immobilization efficiency of BAp.

366 It can be observed that the pH values of SWR significantly increased (from
367 8.48 to 9.80-9.84) after both amendments at 0 year (Figure 4). This increased
368 alkalinity by MgO addition may aid the precipitation of Cd^{2+} and Pb^{2+}.
369 SEM/EDX and XRD tests were conducted trying to identify the formed
370 $Mg(OH)_2$ and metal precipitates. No significant findings can be observed from
371 SEM/EDX results or XRD patterns (Figure S1, S2 and S3), which was likely
372 due to the relatively low concentration and low crystallinity of brucite and its
373 resembling morphology to clay minerals as well as the complex metal
374 precipitates in the soil. The detection limit depends highly on the XRD machine
375 setup and the crystallinity of the minerals formed. Both reactive MgO and the
376 brucite formed usually have low crystallinity (Jin et al., 2014), and thereby

cannot be detected by the current XRD setup at the current concentrations. It is believed that high energy XRD is required to detect the residual MgO and brucite from the mixtures which warrants further studies.

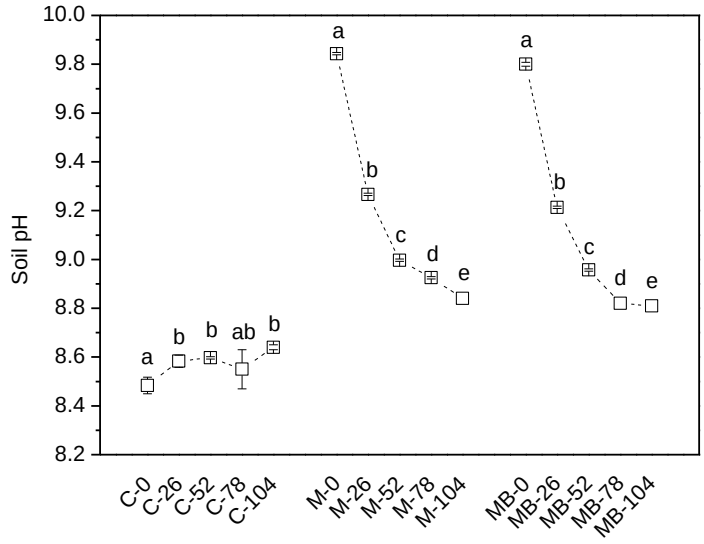
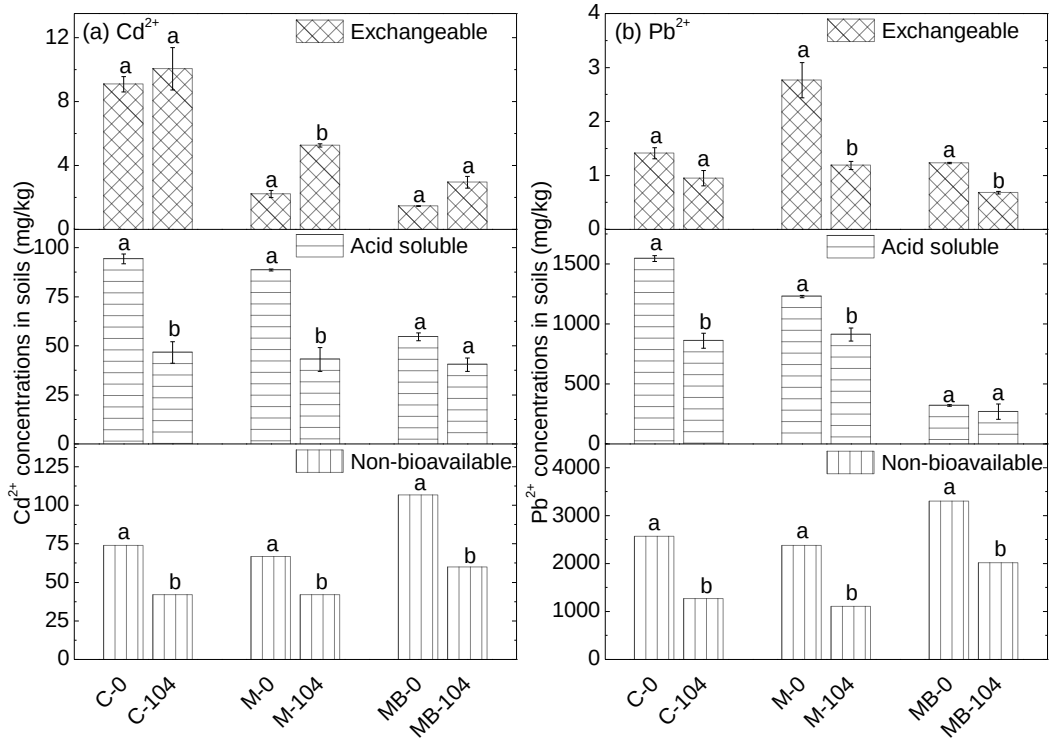


Figure 4. Soil pH values in original and amended soil washing residues (C – control, M – 5% MgO, MB – 5% MgO + 5% Bioapatite; 26, 52, 78 and 104 indicate the simulated years in field conditions; 0 means after immediate treatment; different lower-case letters indicate significant differences between two data groups)

3.4 Effect of accelerated ageing

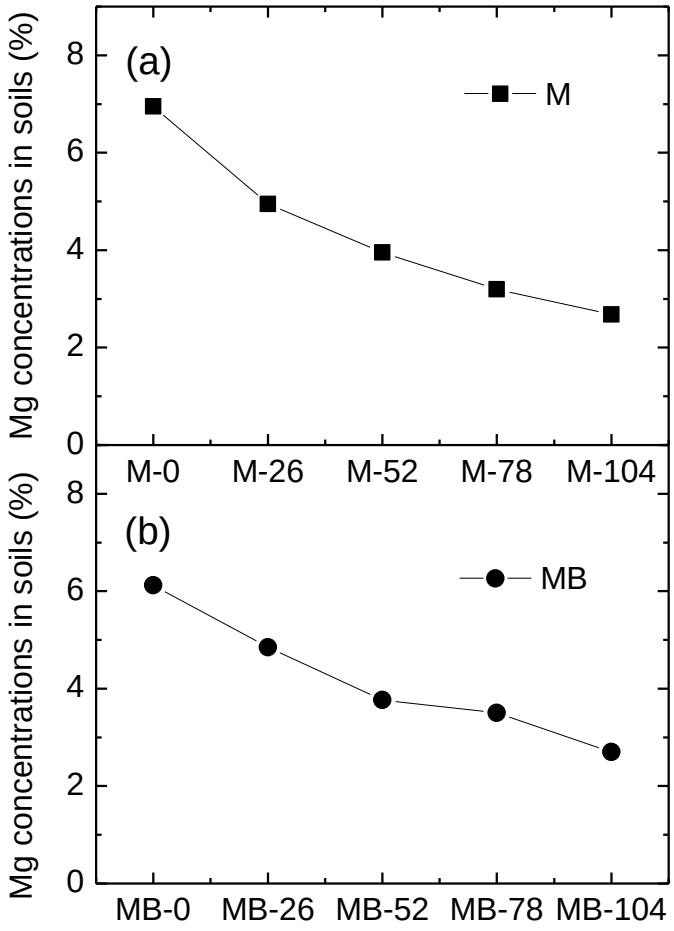
Accelerated aging significantly mobilized Cd^{2+} and Pb^{2+} (Figure 1) and leached out a large amount of Cd^{2+} and Pb^{2+} in the original and amended SWRs (Figure 2). Figure 5 shows the variation of the fractions of Cd^{2+} and Pb^{2+} in soils at 0 year and 104 years. It can be observed that, at simulated 104 years,

391 significant amounts of Cd^{2+} in acid soluble and non-bioavailable fractions of all
392 samples were leached out, whereas the exchangeable factions increased due
393 to the mobilization by accelerated ageing. In comparison, exchangeable, acid
394 soluble and non-bioavailable Pb^{2+} all decreased in the samples. This may be
395 due to that the relative stable fractions of Cd^{2+} and Pb^{2+} were simultaneously
396 leached out by accelerated ageing; or the weakly bound metals were leached
397 out first and those in more stable forms were mobilized and redistributed into
398 weak forms. The leaching dynamics of exchangeable Cd^{2+} and Pb^{2+} seem
399 dependent on the metal type. XRD tests were performed (Figure S2 and S3),
400 however no significant hints were observed. Figure 6 shows the decrease of
401 Mg in both treated SWRs, suggesting continuous dissolution and release of
402 MgO/brucite by the accelerated ageing across 104 years. This again suggests
403 the long-term uncertainty of the stabilization.



404

405 Figure 5. Cd^{2+} and Pb^{2+} concentrations (mg/kg) in each fraction of original and
406 amended soil washing residues at 0-year and 104-year (C – control, M – 5%
407 MgO, MB – 5% MgO + 5% Bioapatite; 0 and 104 indicate the simulated years
408 in field conditions under natural rain; different lower-case letters indicate
409 significant differences between two data groups).



410

411 Figure 6. Mg concentrations in treated soil washing residues across simulated
412 104 years (M – 5% MgO, MB – 5% MgO + 5% Bioapatite; 26, 52, 78 and 104
413 indicate the simulated years in field conditions; 0 means after immediate
414 treatment).

415 3.5 Environmental implications and limitations

416 This study shows that MgO and MgO + BAp amendments both effectively
417 immobilized the Pb^{2+} and Cd^{2+} to below their respective TCLP regulatory levels

418 within simulated 26 years. At simulated 52 years and later, the metals were
419 significantly mobilized – Cd^{2+} in both amended SWRs exceeded the TCLP
420 regulatory level; TCLP leached Pb^{2+} also significantly increased. Also, the total
421 metal concentrations in the amended SWRs slightly reduced at simulated 52
422 years and dramatically reduced from simulated 52 to 104 years. This suggests
423 that the effectiveness of both amendments cannot be retained at simulated 52
424 years. The diminishing long-term effectiveness may result in higher life cycle
425 secondary impact of remediation operation (Hou et al., 2018), inappropriate
426 cleanup standard (Hou et al., 2017b), and diminished the overall sustainability
427 (Hou et al., 2017a).

428 Limited field-monitoring was performed for long-term assessment of
429 stabilization of a contaminated site. A 5-year effectiveness of biochar
430 amendment was observed for Cd^{2+} and Pb^{2+} immobilization in a paddy soil
431 (Cui et al., 2016). Similarly, cement-based S/S was found to successfully
432 stabilized metals in an industrial contaminated site in a 17-year study (Wang et
433 al., 2014). Therefore, the observed 26 years of effective duration for both
434 amendments represent a good long-term performance. This was due to the
435 low solubility of MgO and its hydration products ($Mg(OH)_2$) as well as the low
436 solubility of BAp (Chimenos and Fern, 2004; Wang et al., 2016; Z. Li et al.,
437 2017). The slower release of the binders under rain wash, the longer
438 effectiveness can be reached.

439 Pb^{2+} in M at simulated 52 years, and in MB at simulated 52, 78 and 104 years
440 was all below the TCLP regulatory level (Figure 1). This suggests the
441 amended SWRs were safe according to TCLP assessment in terms of Pb^{2+}.
442 However, the total Pb^{2+} concentration results (Figure 2) clearly show that a
443 large amount of Pb^{2+} has been leached out during this period. These leached
444 Pb^{2+} may potentially impose risks to various environmental receptors (e.g.
445 groundwater and surface runoff) if it were in the field.

446 BAp can significantly aid MgO in immobilizing Cd^{2+} and Pb^{2+} in SWR and
447 reduce their concentrations in the TCLP leachates. However, the
448 enhancement cannot offset the mobilization by accelerated ageing in the long
449 term. More effective additives may be considered to aid MgO in soil
450 stabilization of heavy metals. The identification and assessment of such
451 additives is important for effective and sustainable remediation. Such
452 innovative methods have been developed for the remediation of other heavy
453 metals in recent years (Ma et al., 2015, 2014), which renders implications for
454 developing new additives for stabilization.

455 It is of note that the ageing method used in this study has not been verified and
456 compared with field monitoring. Field application of stabilization reagents has
457 many challenges (O'Connor et al., 2018). In field conditions, the retention time
458 of rain water in the soil profile depends on soil's hydraulic conductivity. The
459 retention time of rain water in upper soil may be relatively short due to the large

porosity and high hydraulic conductivity. Therefore, the upper soil may not react with H^+ from rain water sufficiently. In this laboratory ageing tests, the soil was mixed and stirred with simulated rain water. The reaction between the soil and H^+ is likely more thorough than that in field conditions. In addition, the drying process was performed at 40°C, the temperature of which was higher than typical conditions in the field. Therefore, the ageing methods may simulate more aggressive conditions than in the field. Considering this aspect, the observed effective duration of 26 years for the amendments is likely conservative. However, other factors in the field (e.g., soil texture, ultraviolet radiation, microbial activity, temperature changes and human activities) may also contribute to the ageing of the stabilized soil. Therefore, it is postulated that long-term field monitoring should be carried out to verify the appropriateness of this laboratory accelerated ageing test.

4 Conclusions

This study observed that MgO and MgO + BAp amendments both effectively immobilized Cd^{2+} and Pb^{2+} in the SWR and reduced the risk of the SWR to below the TCLP regulatory levels within simulated 26 years under the accelerated aging condition. At simulated 52 years, the TCLP leached Cd^{2+} from M and MB exceeded regulatory level. At simulated 104 years, the TCLP leached Cd^{2+} from M and MB exceeded regulatory level; TCLP leached Pb^{2+} from M exceeded regulatory level. Large amounts of Cd^{2+} and Pb^{2+} were

leached out regardless of the treatments at simulated 104 years. This study suggests that the effectiveness of both amendments can be retained within simulated 26 years. BAp can significantly aid MgO in metal stabilization, however, the both stabilization diminished at simulated 52 years and from 52 to 104 years. This study also shows that the developed ageing method is able to assess the stability of metals in soils across a long term. Field monitoring is encouraged to correlate and verify the findings from this accelerated ageing experiments.

Acknowledgements

This work was supported by the National Water Pollution Control and Treatment Science and Technology Major Project (No. 2018ZX07109-003) and the National Natural Science Foundation of China (Grant No. 41671316). Moreover, this study was partly funded by the Thousand Talents Program of the Chinese government and Tsinghua University. The first author would like to thank the Killam Trusts of Canada for kindly providing the Izaak Walton Killam Memorial Postdoctoral Fellowship.

References

Chimenos, J.M., Fern, A.I., 2004. Low-grade MgO used to stabilize heavy metals in highly contaminated soils 56, 481–491. doi:10.1016/j.chemosphere.2004.04.005

501 Cui, L., Pan, G., Li, L., Bian, R., Liu, X., Yan, J., Quan, G., Ding, C., Chen, T.,
502 Liu, Y., others, 2016. Continuous immobilization of cadmium and lead in
503 biochar amended contaminated paddy soil: A five-year field experiment.
504 Ecol. Eng. 93, 1–8.

505 Dermont, G., Bergeron, M., Mercier, G., Richer-Laflèche, M., 2008. Soil
506 washing for metal removal: A review of physical/chemical technologies
507 and field applications. J. Hazard. Mater. 152, 1–31.
508 doi:10.1016/j.jhazmat.2007.10.043

509 Du, E., Dong, D., Zeng, X., Sun, Z., Jiang, X., de Vries, W., 2017. Direct effect
510 of acid rain on leaf chlorophyll content of terrestrial plants in China. Sci.
511 Total Environ. 605, 764–769.

512 Griffiths, R.A., 1995. Soil-washing technology and practice. J. Hazard. Mater.
513 40, 175–189. doi:10.1016/0304-3894(94)00064-N

514 Hale, S.E., Hanley, K., Lehmann, J., Zimmerman, A., Cornelissen, G., 2011.
515 Effects of chemical, biological, and physical aging as well as soil addition
516 on the sorption of pyrene to activated carbon and biochar. Environ. Sci.
517 Technol. 45, 10445–53. doi:10.1021/es202970x

518 Hou, D., Al-Tabbaa, A., 2014. Sustainability: A new imperative in contaminated
519 land remediation. Environ. Sci. Policy 39, 25–34.
520 doi:10.1016/j.envsci.2014.02.003

521 Hou, D., Al-Tabbaa, A., Hellings, J., 2015. Sustainable site clean-up from
522 megaprojects: lessons from London 2012. Proc. Inst. Civ. Eng. - Eng.
523 Sustain. 168, 61–70. doi:10.1680/ensu.14.00025

524 Hou, D., Ding, Z., Li, G., Wu, L., Hu, P., Guo, G., Wang, X., Ma, Y., O'Connor,
525 D., Wang, X., 2017a. A Sustainability Assessment Framework for
526 Agricultural Land Remediation in China. L. Degrad. Dev.
527 doi:10.1002/ldr.2748

528 Hou, D., Qi, S., Zhao, B., Rigby, M., O'Connor, D., 2017b. Incorporating life
529 cycle assessment with health risk assessment to select the 'greenest'
530 cleanup level for Pb contaminated soil. J. Clean. Prod. 162, 1157–1168.
531 doi:10.1016/j.jclepro.2017.06.135

532 Hou, D., Song, Y., Zhang, J., Hou, M., O'Connor, D., Harclerode, M., 2018.
533 Climate change mitigation potential of contaminated land redevelopment:
534 A city-level assessment method. J. Clean. Prod. 171, 1396–1406.

535 Jin, F., Al-Tabbaa, A., 2014. Characterisation of different commercial reactive
536 magnesia. Adv. Cem. Res. 26, 101–113.

537 Jin, F., Gu, K., Abdollahzadeh, A., Al-Tabbaa, A., 2013. Effects of different
538 reactive MgOs on the hydration of MgO-activated GGBS paste. J. Mater.
539 Civ. Eng. 27, B4014001.

540 Jin, F., Gu, K., Al-Tabbaa, A., 2014. Strength and drying shrinkage of reactive

MgO modified alkali-activated slag paste. Constr. Build. Mater. 51, 395–404. doi:10.1016/j.conbuildmat.2013.10.081

Li, Q., Lu, L., Xie, S., Zhang, P., Wang, S., Zhang, X., Zhou, Z., Li, Z., 2017. Mineralogical changes of bioapatite in femoral bones of mice during pregnancy. Spectrosc. Lett. 50, 336–341. doi:10.1080/00387010.2017.1329213

Li, Z., Tang, L., Zheng, Y., Tian, D., Su, M., Zhang, F., Ma, S., Hu, S., 2017. Characterizing the Mechanisms of Lead Immobilization via Bioapatite and Various Clay Minerals. doi:10.1021/acsearthspacechem.7b00016

Ma, F., Peng, C., Hou, D., Wu, B., Zhang, Q., Li, F., Gu, Q., 2015. Citric acid facilitated thermal treatment: An innovative method for the remediation of mercury contaminated soil. J. Hazard. Mater. 300, 546–552. doi:10.1016/j.jhazmat.2015.07.055

Ma, F., Zhang, Q., Xu, D., Hou, D., Li, F., Gu, Q., 2014. Mercury removal from contaminated soil by thermal treatment with FeCl3 at reduced temperature. Chemosphere 117, 388–393. doi:10.1016/j.chemosphere.2014.08.012

O'Connor, D., Peng, T., Zhang, J., Tsang, D.C.W., Alessi, D.S., Shen, Z., Bolan, N.S., Hou, D., 2018. Biochar application for the remediation of heavy metal polluted land: A review of in situ field trials. Sci. Total Environ.

619–620, 815–826. doi:10.1016/j.scitotenv.2017.11.132

Oustriere, N., Marchand, L., Lottier, N., Motelica, M., Mench, M., 2016. Long-term Cu stabilization and biomass yields of Giant reed and poplar after adding a biochar, alone or with iron grit, into a contaminated soil from a wood preservation site. Sci. Total Environ. 579, 620–627. doi:10.1016/j.scitotenv.2016.11.048

Rechberger, M. V., Kloss, S., Rennhofer, H., Tintner, J., Watzinger, A., Soja, G., Lichtenegger, H., Zehetner, F., 2017. Changes in biochar physical and chemical properties: Accelerated biochar aging in an acidic soil. Carbon N. Y. doi:10.1016/j.carbon.2016.12.096

Sanderson, P., Naidu, R., Bolan, N., Lim, J.E., Ok, Y.S., 2015. Chemical stabilisation of lead in shooting range soils with phosphate and magnesium oxide: Synchrotron investigation. J. Hazard. Mater. 299, 395–403. doi:10.1016/j.jhazmat.2015.06.056

Shen, Z., Hou, D., Zhao, B., Xu, W., Ok, Y.S., Bolan, N.S., Alessi, D.S., 2018a. Stability of heavy metals in soil washing residue with and without biochar addition under accelerated ageing. Sci. Total Environ. 619–620, 185–193. doi:10.1016/j.scitotenv.2017.11.038

Shen, Z., McMillan, O., Jin, F., Al-Tabbaa, A., 2016a. Salisbury biochar did not affect the mobility or speciation of lead in kaolin in a short-term laboratory

study. J. Hazard. Mater. 316, 214–220. doi:10.1016/j.jhazmat.2016.05.042

Shen, Z., Som, A.M., Wang, F., Jin, F., McMillan, O., Al-Tabbaa, A., 2016b. Long-term impact of biochar on the immobilisation of nickel (II) and zinc (II) and the revegetation of a contaminated site. Sci. Total Environ. 542, 771–776. doi:10.1016/j.scitotenv.2015.10.057

Shen, Z., Tian, D., Zhang, X., Tang, L., Su, M., Zhang, L., Li, Z., Hu, S., Hou, D., 2018b. Mechanisms of biochar assisted immobilization of Pb 2+ by bioapatite in aqueous solution. Chemosphere 190, 260–266. doi:10.1016/j.chemosphere.2017.09.140

Shen, Z., Zhang, Y., Jin, F., McMillan, O., Al-Tabbaa, A., 2017b. Qualitative and quantitative characterisation of adsorption mechanisms of lead on four biochars. Sci. Total Environ. 609, 1401–1410.

Sneddon, I.R., Orueetxebarria, M., Hodson, M.E., Schofield, P.F., Valsami-Jones, E., 2006. Use of bone meal amendments to immobilise Pb, Zn and Cd in soil: A leaching column study. Environ. Pollut. 144, 816–825. doi:10.1016/j.envpol.2006.02.008

Song, Y., Hou, D., Zhang, J., O'Connor, D., Li, G., Gu, Q., Li, S., Liu, P., 2018. Environmental and socio-economic sustainability appraisal of contaminated land remediation strategies: A case study at a mega-site in

China. Sci. Total Environ. 610–611, 391–401. doi:10.1016/j.scitotenv.2017.08.016

Suzuki, T., Nakamura, A., Niinae, M., Nakata, H., Fujii, H., Tasaka, Y., 2013. Lead immobilization in artificially contaminated kaolinite using magnesium oxide-based materials : Immobilization mechanisms and long-term evaluation. Chem. Eng. J. 232, 380–387. doi:10.1016/j.cej.2013.07.121

Wang, F., Jin, F., Shen, Z., Al-Tabbaa, A., 2016. Three-year performance of in-situ mass stabilised contaminated site soils using MgO-bearing binders. J. Hazard. Mater. 318, 302–307.

Wang, F., Wang, H., Al-Tabbaa, A., 2014. Leachability and heavy metal speciation of 17-year old stabilised/solidified contaminated site soils. J. Hazard. Mater. 278, 144–151.